

**Pyrolysis DART-MS Analysis of Ignitable Liquids for Forensic and Environmental  
Applications**

by

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fulfillment of the requirements for graduation from the University Honors College

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## ABSTRACT

Conventional Gas Chromatography/Mass Spectrometry (GC/MS) methods for the analysis of ignitable liquids (ILs) are usually time-consuming and the data produced are difficult to interpret. A fast IL screening method using direct analysis in real time mass spectrometry (DART-MS) is proposed in this study. QuickStrip DART-MS and thermal desorption DART-MS methods were used to analyze neat ILs and thermal desorption DART-MS, without extraction, was used to analyze ILs on five substrates (e.g., carpet, wood, cloth, sand, and paper). Compared to GC/MS, DART-MS methods generated different spectral profiles for neat ILs with more peaks in the higher mass range and also provided better detection of less volatile compounds. ILs on substrates were successfully classified ( $98 \pm 1\%$ ) using partial least squares discriminant analysis (PLS-DA) models based on thermal desorption DART-MS data. This study shows that DART-MS has great potential for the high throughput screening of ILs on substrates.

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## INTRODUCTION

Over the years, it has been of great interest to researchers in forensic and environmental science for the characterization of petroleum-based fuels. In the context of forensic arson investigations, fuels such as gasoline, kerosene, and diesel are the most commonly encountered accelerants to increase the rate and spread of the fire.[1] The evidential link between a suspect and a crime scene could be established based on the identification of these fuels and/or the source of them. American Society for Testing and Materials (ASTM) E1618 gas chromatography-mass spectrometry (GC-MS) method is commonly used for the analysis of these petroleum-based ignitable liquids.[2] However, this methodology is time-consuming and subject to the skill and experience of analyst.

Ambient mass spectrometry methods such as direct analysis in real time mass spectrometry (DART-MS) can be an alternative method for petroleum product identification which enables the direct sample analysis without chromatographic separation steps.[3, 4] DART-MS method requires limited sample preparation and is applicable to the analysis of both volatile and nonvolatile compounds with excellent analytical sensitivity.[5] The objective of this research is to distinguish among different classes of ignitable liquid samples by using DART-MS technique, a thermal desorption module, and chemometrics. The concentration is on analyzing the effects and reliability of the IonRocket system, a pyrolysis device to couple with DART-MS to assist in analysis, especially with samples on substrates. Conducting this research may provide significant data to advocate for the use of the DART-MS method and IonRocket system, over current

methods, in future analysis within multiple areas of study, including forensic and environmental science.

## BACKGROUND

A case study analyzed over 100 crude oils and refined petroleum products, including gasoline, kerosene, and diesel, and found that chemical profiles were similar in oils from the same area, but varied from different areas.[6, 7] This is not unexpected because gasoline and other petroleum products are produced from crude oil by refineries and most gasoline/diesel is sent from refineries to large storage terminals near consuming areas through shared pipelines, where commingling occurs, and then delivered by truck to the fueling station. However, the proprietary additives blended into the gasoline/diesel before it enters the fueling stations are different from one company to another.[8] Detergents such as polyisobutene (PIB) succinimides and polyether amines are commonly added into both gasoline and diesel fuels to control the deposits.[9, 10] The profiles of these chemicals could be important markers for gasoline/diesel with different brands. Nevertheless, these detergents cannot be analyzed by the traditional GC-MS methods due to their low concentrations (<0.5%, w/w) [11], low volatility (boiling points >300 °C)[12], high molecular weights, and complexity of polymeric structures.[13]

DART-MS method requires limited sample preparation and is applicable to the analysis of both volatile and nonvolatile compounds with excellent analytical sensitivity especially for nonvolatile and polar fractions.[5] These nonvolatile components have been shown to function as natural markers for petroleum products, such as type, origin, and biodegradation.[14] They are less variable compared to their volatile chemical profiles and are therefore more desirable for yielding reliable and solid evidence in arson investigation. In addition, DART ion source primarily produces protonated molecules ( $[M+H]^+$ ),[15]

which simplifies the data interpretation and can provide detailed and characteristic fingerprints for different petroleum-based fuels.

A pyrolysis device is proposed to couple with DART-MS to assist in the analysis of ignitable liquids. The purpose of the ionRocket system is to vaporize various compounds within samples to give an accurate and comprehensive analysis of substances whose matrixes are too complicated for analysis using only DART-MS. IonRocket system is an ideal unit for the analysis of ignitable liquids with which the samples can be heated up to 600 °C with accurate temperature gradient control for DART-MS analysis. The temperature can be increased at the rate of 100 °C per minute, so data with three dimensions consisting of  $m/z$ , time (=temperature), and intensity will be generated which could further enhance the discriminating power comparing with sole DART-MS analysis when chemometrics is applied. In addition, since certain hydrocarbons in diesel and kerosene have boiling points up to 360 °C, more residues could be observed than analyzed directly by using DART-MS. The IonRocket system with gradient temperature program would also benefit the identification of these heavy petroleum distillates by profiling the compounds with various volatilities. The pyrolysis DART-MS system was used for the classification of various petroleum distillates such as gasoline, kerosene, paint remover, lighter fuel, and so on.

Chemometrics was critical for both data preprocessing and statistical analysis. A commercial chemometric software, SIMCA-P 13.0, was used to perform the data analysis. Fuel additives are complex mixtures and it is not practical and reliable to rely on one or several 'characteristic' ion(s) for the differentiation of gasoline samples especially when many brands are involved. Statistical and chemometric methods have also been widely

used to increase the confidence in the association or discrimination and build more definitive links between samples in forensic research.[16-21] In this study, different data preprocessing techniques such as binning, normalization, scaling, and data transformation were applied and both unsupervised and supervised statistic models such as principal component analysis (PCA), partial least square discriminant analysis (PLS-DA), and soft independent modeling of class analogy (SMICA) were established and validated.

The proposed research will add knowledge to the field of analytical chemistry. The understanding of the chemical profiles of different ignitable liquids can not only assist forensic arson and environmental fuel spill investigation, but can also help assess their impact to the environment, human health, and fuel efficiency. Moreover, although Cody *et al.* have reported several pyrolysis DART-MS studies previously[22-24], this research would be a pioneer for gradient heating controlled pyrolysis DART-MS which will hold great potential across a broad range of topics in the analytical chemistry area.

## MATERIALS

The instruments utilized for this experiment included the DART-MS and ionRocket pyrolysis module for analysis of the samples. The QuickStrip™ Sample Cards were necessary to spot samples and conduct analysis using the DART-MS. For analysis using the ionRocket, the samples were placed in copper sample pots designed specifically for the ionRocket system. The ignitable liquids, including: kerosene, diesel, japan drier, charcoal starter fluid, naphtha, prestain, and lighter fluid, were purchased from local home improvement stores. Several substrates, including: cotton swabs, wood floor samples, paper, clothing swatches, and sand, were used in this experiment. High point chestnut plank flooring and 100% PureColor™ solution dyed BCF polyester carpet were acquired from a local home improvement store. Sand (50–70 mesh particle size) was purchased from Sigma-Aldrich, St. Louis, MO.

## EXPERIMENTAL PROCEDURES

### *Instruments and Parameters*

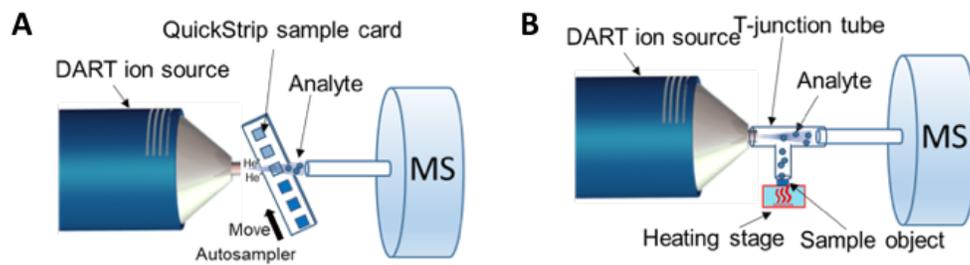
For DART-MS experiments in this study, a DART ion source (IonSense, Inc., Saugus, MA) was coupled to a Thermo LTQ XL mass spectrometer (Thermo Scientific, San Jose, CA). The ionization gas was helium for all the DART-MS experiments. The DART gas heater was set to 350°C, and the mass spectra were collected in an  $m/z$  range of 50–1000 in positive-ion mode. QuickStrip, tweezer, and thermal desorption modules were used in this study for DART-MS analysis. For QuickStrip DART-MS analysis, an automated sample introduction apparatus consisting of a Linear Rail Enclosure that holds QuickStrip™ sample cards was used (IonSense, Inc., Saugus, MA). QuickStrip™ Sample Cards were purchased from IonSense, Inc. (Saugus, MA). The preloaded “QuickStrip” method was used: Heater Wait Time 30 sec; Sample Speed 0.5 mm/sec; Contact Closure Delay 5 sec; Standby Temperature 345 °C. The tweezer module was set up by replacing the QuickStrip sample card holder with a tweezer holder. Most of the DART-MS parameters were the same as the QuickStrip module except the gas heater temperature which was set to 200 °C. For thermal desorption analysis, the IonRocket temperature gradient system provided by BioChromato, Inc. (San Diego, CA) was used for DART-MS. The temperature program used was 25 °C initial, hold for 1 min, ramp at 100 °C/min to 600 °C, hold for 1 min.

For GC-MS analysis, a Shimadzu QP2010S (Shimadzu, Kyoto, Japan) equipped with an auto sampler was used. The GC injector was set at 280 °C and the analytes were separated on a SHRCI-5MS, 30 m × 0.25 mm ID capillary column chemically bonded with

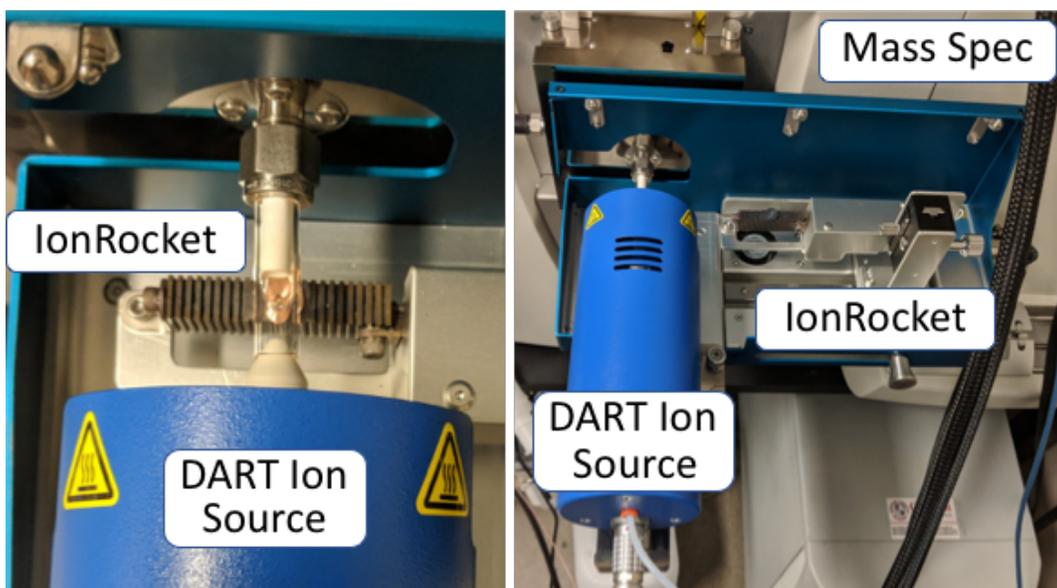
5% diphenyl/95% dimethyl polysiloxane at 0.1  $\mu\text{m}$  film thickness (Shimadzu Scientific Instruments Inc. Columbia, MD). A constant helium flow of 1 mL/min was used, of which a fixed split of approximately 1:50 entered the column. The column temperature was programmed as follows: 50  $^{\circ}\text{C}$ , hold for 1 min, ramp at 20  $^{\circ}\text{C}/\text{min}$  to 280  $^{\circ}\text{C}$ , hold for 10 min. The transfer line and ion source temperatures were both maintained at 280  $^{\circ}\text{C}$ . Full scan mode was selected for the mass spectrometer and the scan range was from  $m/z$  30 to 350.

#### *Analysis of Neat ILs*

Neat ILs were analyzed by QuickStrip DART-MS and thermal desorption DART-MS and the mass spectral profiles using these methods were compared, setups displayed in Figure 1. For QuickStrip DART-MS, 3  $\mu\text{L}$  liquid samples were spotted onto QuickStrip<sup>TM</sup> sample cards in triplicate. Blank spots on each sample card were analyzed for mass spectral background subtraction. For thermal desorption DART-MS, 3  $\mu\text{L}$  liquid samples were loaded onto disposable copper sample pots which were then placed on the heating block. A glass T-junction was positioned over the copper sample pot, and the compounds were thermally desorbed from the samples and then analyzed directly by DART-MS, setup displayed in Figure 2.



**Figure 1.** Sample introducing strategies of the DART-MS. A: QuickStrip module; B: Thermal desorption module.



**Figure 2.** DART-MS and setup thermal desorption method

### *Analysis of ILs on Substrates*

Ignitable liquids on substrates were analyzed using both the tweezer and thermal desorption modules with DART-MS, and the resulting mass spectra were compared to each other and to spectral profiles of neat ILs. Five substrates, including carpet, wood flooring, sand, paper, and T-shirt material (97% cotton and 3% elastane) were tested. Samples were cut and placed directly into the reservoir of the copper sample pot for thermal desorption analysis, except for wood flooring samples. For wood flooring samples, Q-swabs were used to collect the residue of ILs from the surface of the flooring, and then the tips were cut off and analyzed in the copper sample pots. A blank was run for each substrate to determine which peaks from the DART-MS could be attributed to the substrate, and which were due to the ignitable liquid. Each sample was run in triplicate to analyze reproducibility and to develop a robust method. When using the tweezer module, each sample was held by a clean tweezer which was then placed onto the tweezer holder for DART-MS analysis.

### *Data Format*

For data collected by DART-MS analysis with QuickStrip and tweezer modules, the background spectrum was first subtracted then the average mass spectrum for each sample was exported to Excel with Xcalibur 2.1 software (Thermo Scientific, Waltham, MA). For data collected by thermal desorption DART-MS analysis, the average mass spectra of desired time/temperature windows were exported to Excel without background subtraction. The data were binned by  $m/z$  from 50 to 1000 with 0.5 increments and then normalized to unit vector length [25] for further chemometric analysis in SIMCA-P

(version 13.0 Umetrics, Sweden). MATLAB R2017a (MathWorks Inc., Natick, MA) was used for validation of the chemometric models.

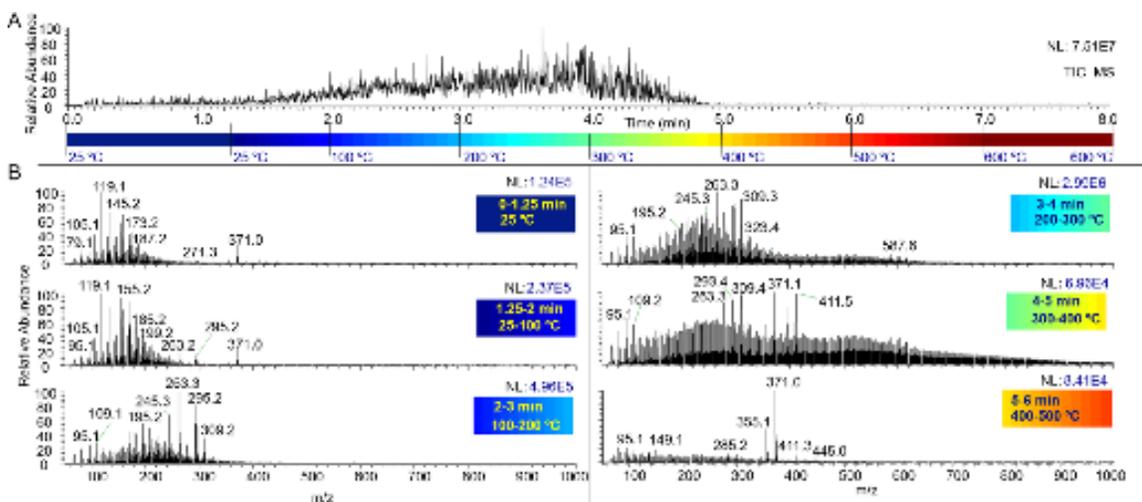
## RESULTS AND DISCUSSION

### *Comparison of DART-MS and GC-MS Data for Neat IL Analysis*

Comparable results were achieved for all of the ILs in the study when comparing GC-MS and DART-MS mass spectral profiles. The DART-MS spectral profiles were very different from GC-MS spectral profiles and more characteristic ions were found in thermal desorption DART-MS spectra than in Quick-Strip DART-MS spectra. A representative thermal desorption DART-MS TIC, total ion current, for kerosene is shown in Fig. 3A and the average mass spectra for different time windows are shown in Fig. 3B. Similar to the QuickStrip DART-MS data, higher masses ( $>m/z$  100) were found in these mass spectra relative to the GC-MS data and most of the ions in the QuickStrip DART-MS spectra can also be observed in thermal desorption DART-MS spectra.

Furthermore, more compounds were detected and significantly different profiles were observed with respect to the temperature gradient in thermal desorption DART-MS spectra. From 0 to 1 min, the sample pot was unheated, so only highly volatile compounds were detected by the mass spectrometer. The resulting mass spectrum consisted of clusters of peaks with differences of 14 Da. From 1 to 2 min, more peaks appeared as the sample pot started to heat (100 °C/min from 25 °C). For example,  $m/z$  263.2 and 295.2 were emerging in this temperature range and both peaks also existed in the QuickStrip DART-MS spectra. From 2 to 3 min (100 to 200 °C),  $m/z$  263.2 and 295.2 and several new peaks became major peaks in the mass spectrum and  $m/z$  309.2 started to emerge. From 3 to 4 min (200 to 300 °C),  $m/z$  309.2 became one of the highest peaks in the mass spectrum and additional higher mass peaks ( $>m/z$  350) also came out at this temperature window. As the

temperature continued to increase, there was a relative decrease in the abundance of lower mass peaks and increase in higher mass peaks. In general, peaks with lower masses were mainly observed at lower temperatures and compounds with higher masses were identified at higher temperature in thermal desorption DART-MS spectra. This observation agrees with the common rule for organic molecules: for molecules with a given functional group, boiling point increases with molecular weight.



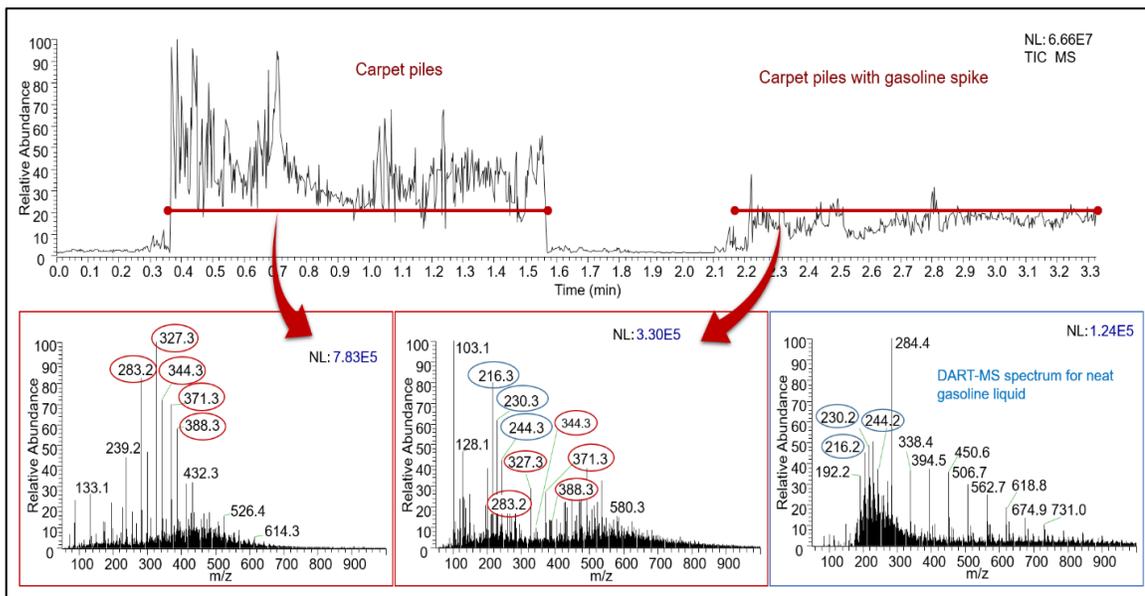
**Figure 3.** Analysis of kerosene by thermal desorption DART-MS: TIC (A) and mass spectra for different time/temperature windows (B).

### *Interferences of Substrate Matrix*

*Tweezer Module with DART-MS*—Figure 4 shows the average mass spectra for neat gasoline analyzed by QuickStrip DART-MS, and blank carpet piles and carpet piles with gasoline spikes analyzed by DART-MS with the tweezer module. The carpet used in this study was made of polyester and ion clusters with 44 Da repeating units were formed in the mass spectra. There are two clusters of ions in the DART-MS spectrum for gasoline neat liquid:  $m/z$  202.2–272.2 with 14 Da repeat units and  $m/z$  284.4–956.4 with 56 and 58 Da repeat units. For gasoline spiked carpet piles, characteristic ions for carpet including  $m/z$  283.2, 327.3, 344.3, 371.3, and 388.3, and ions for gasoline such as  $m/z$  216.2, 230.2, and 244.2 were detected. The other set of characteristic ions with the 56 and 58 Da repeat units found in gasoline neat liquid samples were not seen in this mass spectrum. These ions, corresponding to proprietary fuel additives, are important characteristic features for gasoline, and they were found to be gasoline brand dependent.[26]

There are several possible reasons for not detecting fuel additive ions. First, the boiling points of fuel additives such as polyisobutene (PIB) succinimides and polyether amines are usually higher than 250 °C [12] and the temperature of the helium gas stream decreases dramatically with increasing sample gap distance when using the tweezer module. Second, these polymeric additives may tend to bond to the polymer of carpet fibers, which makes it even harder to be detected. In addition, ion suppression effect was observed in this study and less volatile fuel additives could be suppressed more significantly than the volatile compounds. The volatile compounds are expected to be ionized faster, since they can be released from substrates more easily.

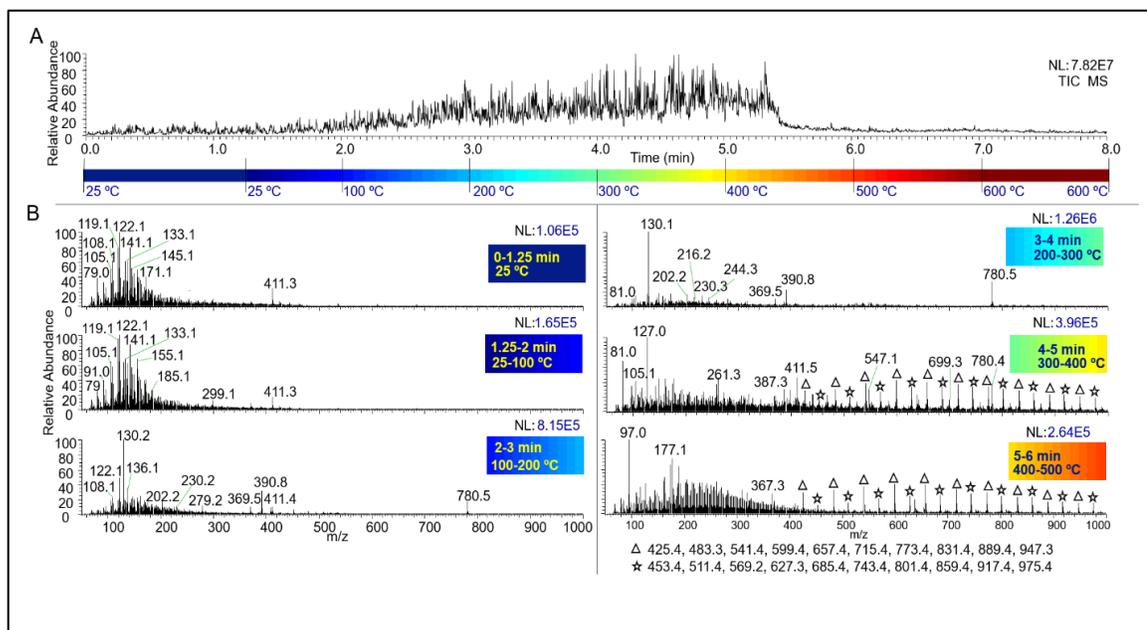
Similar interference from the carpet matrix was found with other ILs. Background spectral subtraction is critical to observe the characteristic peaks in some IL samples. For example, when spiked onto carpet, the characteristic ions such as  $m/z$  277.3 and 319.4 for Gulf Charcoal Starter cannot be observed because ions from carpet fibers dominate the spectrum. However, the characteristic ions stand out after subtracting the mass spectrum for blank carpet fibers (Figure 4). Background subtraction is important especially for the analysis of trace levels of ILs or ILs with low volatility when using the DART-MS tweezer module.



**Figure 4.** Gasoline on Carpet Substrate by DART-MS with tweezer module. Top: TIC. Bottom: Mass spectra for blank carpet piles, carpet piles with gasoline spike, and neat gasoline liquid.

The major difficulty observed when using DART-MS with the tweezer module was the immobilization of substrates, such as sand and carpet, in the helium stream between the DART ion source and MS orifice. Another concern was the fact that fine fibers from carpet or fine sand particles might accumulate at or even fly into the ion transfer capillary of the mass spectrometer which would contaminate and damage the instrument. In addition, the tweezer module for the DART ion source was able to hold the sample object at a relatively consistent position, however, the irregular shapes of sample objects disturbed the helium flow and affected the analysis.

*Thermal Desorption DART-MS*—For neat gasoline analyzed by thermal desorption DART-MS, there were three groups of characteristic peaks: a) a group of volatile compounds with 14 Da repeat units which were detected at room temperature, for example,  $m/z$  91.0, 105.1, 119.1, and 133.1; b) another group of compounds with 14 Da repeat units which were usually detected between 200 to 300 °C, for example,  $m/z$  202.2, 216.2, 230.3, and 244.3; and c) fuel additives such as fuel detergent peaks which were commonly detected between 320 to 450 °C, for example,  $m/z$  627.3, 685.4, 743.4, and 801.4. Figure 5 shows the results of thermal desorption DART-MS analysis for gasoline residues on wood flooring. All three groups of compounds were detected at different temperatures. However, only some of these characteristic ions can be detected on carpet substrate. The polyester carpet fibers started to pyrolyze at 300 °C, therefore, peaks in group c were suppressed by the dominant peaks from pyrolyzed polyester in the mass spectra.



**Figure 5.** Analysis of gasoline residues on wood floor substrate by the thermal desorption DART-MS: TIC (A) and mass spectra for at different time/temperature windows (B).

Note: Two clusters of peaks associated with fuel additive compounds are labeled with triangles and stars.

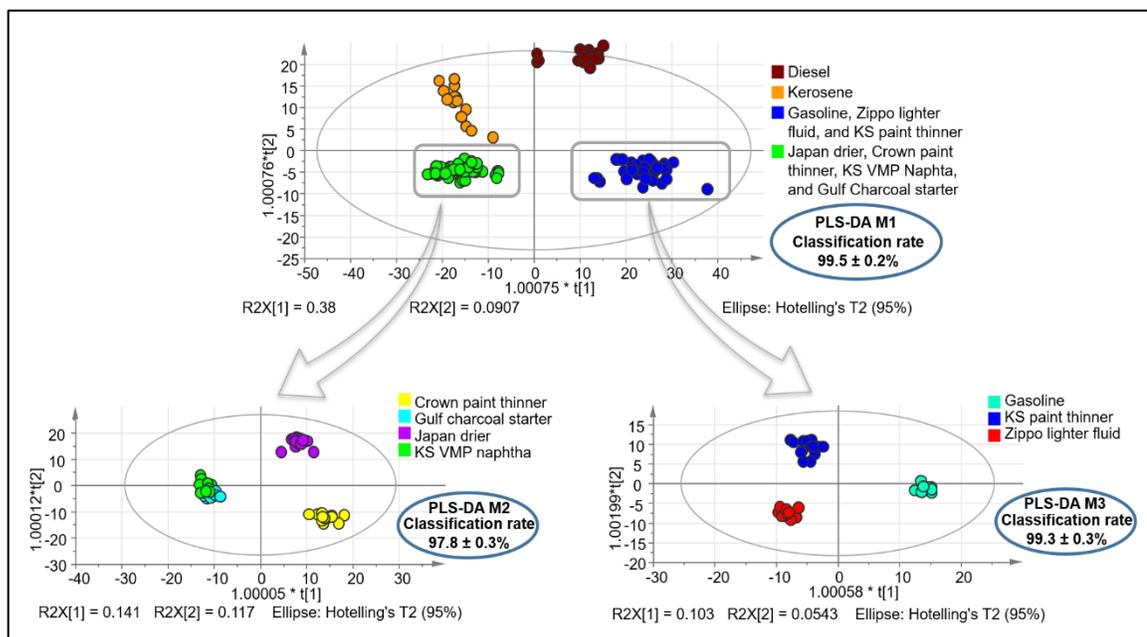
All three groups of gasoline characteristic ions were found in the mass spectra of the other four substrates analyzed by thermal desorption DART-MS. The substrates interfered with the gasoline residue results differently, dependent on the complexity of compounds released from the substrate materials at different temperatures. The coexisting compounds from the substrate can suppress or mask the signals of targeted ions originated from ILs and complicate the mass spectra. The peaks at the lower mass range were found to be more susceptible to interference. Generally, the clustered ions in the high-mass range,

such as fuel additive ions, are easier to observe and more reliable as evidence for gasoline residues on substrates, if available. The other ILs were also analyzed on different substrates by using thermal desorption DART-MS, and similar success was achieved. The characteristic ions are dependent on the types of the substrates and the DART-MS modules. Therefore, the use of a combination of multiple characteristic ions for the identification of ILs is more reliable than relying on a single ion.

Compared with QuickStrip DART-MS, there are several advantages to the direct analysis of ILs on substrates by thermal desorption DART-MS. First, more types of substrates can be analyzed directly regardless of their shapes and materials as long as they can be cut into small pieces. Since the sample objects are not directly in contact with the helium gas stream from the DART ion source, the immobilization of the samples is easier. Second, similar to GC-MS, the thermal desorption DART-MS provides information associated with chemical volatilities in the data, which could aid in confirming or refuting ambiguous signals for the identification of ILs. Third, more characteristic features can be detected with stronger signals which can be critical in the case where an IL is present at a very low concentration. The compounds on the substrates are separated and analyzed based on volatility and boiling points, therefore, the ion suppression effect for the analytes is less when compared with QuickStrip DART-MS. Fourth, the sample introduction process is more friendly to the mass spectrometer. The sample objects are not exposed directly in front of orifice of the mass spectrometer, so it is unlikely to contaminate the MS instrument. Finally, the temperature of the thermal desorption device can be set up to 600 °C, which enables the detection of less volatile compounds in ILs on substrates, such as fuel additives in gasoline.

### *Classification of IL with the Interference of Substrates*

All nine ILs on five different substrates (e.g., carpet, wood flooring, sand, paper, and T-shirt material) were analyzed using thermal desorption DART-MS, in triplicate. In total there were 133 data objects for chemometric analysis. A multistep classification strategy was adopted for this study because it was found to be more effective at teasing out the differences in the features among objects that belonged to different classes (Fig. 6). Four Latin partitions were bootstrapped 100 times to evaluate the partial least squares discriminant analysis (PLS-DA) models and the pooled classification rates with 95% confidence intervals were calculated by averaging across the 100 bootstraps.



**Figure 6.** Multistep classification with PLS-DA models for ILs on substrates.

(Classification rates with 95% confidence intervals were obtained from 100 bootstrapped Latin partitions).

The classification results are summarized in Table 1. The overall classification rates for all ILs are above 95%, and the interference of substrate matrices is dependent on the types of substrates and ILs. For KS paint thinner, kerosene, and diesel, 100% classification rates were achieved no matter the types of substrates tested. The classification of gasoline and Zippo lighter fluid was significantly undermined by the interference of carpet matrices with classification rates of  $70 \pm 9\%$  and  $84 \pm 7\%$ , respectively. Polyester peaks from carpet fibers caused serious interference for characteristic peaks in gasoline DART-MS spectra, especially the fuel additive peaks. For carpet substrates, the mass peaks for the compounds

in ILs which were desorbed at 300°C or higher were significantly suppressed by pyrolyzed polyester from carpet. KS VMP naphtha and Gulf charcoal starter tend to be misclassified to one another on paper substrates with classification rates of  $74 \pm 4\%$  and  $88 \pm 6\%$ , respectively. However, both ILs were accurately classified with the interference of the other four substrates ( $\geq 99\%$  classification rates). In addition, 96% classification rates were achieved for all the ILs on wood floor, T-shirt material, or sand substrates. To conclude, classification of ILs using PLS-DA models with thermal desorption DART-MS data, even with the interference of different substrates, demonstrated promising results with an overall classification rate of  $98 \pm 1\%$ .

**Table 1.** PLS-DA classification for the data of 9 ILs on 5 substrates analyzed by thermal desorption DART-MS. Classification rates with 95% confident intervals obtained by 100 bootstrapped Latin partitions

IL names	IL Type*	Carpet	Wood floor	Paper	T-Shirt	Sand	Overall
KS VMP naphtha	LPD	100 ± 0	100 ± 0	74 ± 4	99 ± 1	100 ± 0	95 ± 13
Gulf charcoal starter	LPD	99 ± 1	99.7±0.7	88 ± 6	100 ± 0	100 ± 0	97 ± 6
Zippo lighter fluid	LPD	84 ± 7	100 ± 0	100 ± 0	100 ± 0	100 ± 0	97 ± 8
Crown paint thinner	MPD	100 ± 0	96 ± 2	100 ± 0	100 ± 0	100 ± 0	99 ± 2
KS paint thinner	MPD	100 ± 0	100 ± 0	100 ± 0	100 ± 0	100 ± 0	100 ± 0
Japan drier	MPD	100 ± 0	99.7±0.7	99.7±0.7	100 ± 0	100 ± 0	99.6±0.2
Kerosene	HPD	100 ± 0	100 ± 0	100 ± 0	100 ± 0	100 ± 0	100 ± 0
Diesel	HPD	100 ± 0	100 ± 0	100 ± 0	100 ± 0	100 ± 0	100 ± 0
Gasoline	GAS	70 ± 9	100 ± 0	100 ± 0	100 ± 0	100 ± 0	96 ± 15
Overall		95 ± 8	99.5±0.9	96 ± 6	99.9±0.2	100 ± 0	98 ± 1

\* LPD: light petroleum distillates; MPD: medium petroleum distillates; HPD: heavy petroleum distillates.

## CONCLUSIONS

In this study, it was demonstrated that DART-MS can be used to analyze IL residues on substrates without complicated extraction and chromatographic separation, which could significantly increase sample throughput and simplify interlaboratory comparisons. QuickStrip DART-MS was found to be effective when analyzing neat ILs, while analysis of ILs on substrates by DART-MS with the tweezer module was found to be hampered by background interference as well as potential contamination of the instrument. Thermal desorption DART-MS demonstrated the potential for the detection of neat ILs and IL residues even with the interference of different substrates. Also, ILs on substrates were successfully classified using PLS-DA models with thermal desorption DART-MS data with an overall classification rate at  $98 \pm 1\%$ . Compared with traditional GC-MS methods, this method is fast, simple, and reproducible, allowing for easy comparisons and interpretation between samples. Based on the results presented, DART-MS shows great potential for the high-throughput analysis of various types of ILs on different substrates.

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